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Susceptibility of a heterogeneous catalyst, Rh/γ-alumina, to rapid structural change by exposure to NO†

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Received (in Cambridge, UK) 27th July 2001, Accepted 10th December 2001
First published as an Advance Article on the web 23rd January 2002

Metal particles in a Rh/γ-Al_2O_3 catalyst of differing particle size are oxidised by NO/He within 5 seconds at 313 K; rapid, highly exothermic dissociative chemisorption of NO is the initial step.

The performance of rhodium-containing catalysts to facilitate chemical processes such as CO oxidation and hydrogenation, and also NO reduction using CO, H_2, and hydrocarbons is very dependent upon reaction conditions. We have previously demonstrated that Energy Dispersive EXAFS (EDE) can be used to monitor the formation of metal particles *in situ*, in this case from reduction of $Pt(acac)_2/H_1–SiO_2$.[1] Used in combination with mass spectrometry, the available time resolution allows a direct correlation between structural changes at the metal centres and gas phase composition; in that example, the reaction studied was between NO and $RhCl(CO)_2$/γ-Al_2O_3.[2] In this report, we apply these techniques to investigate the effects of CO and NO, key elements of automotive exhaust catalysis, on the local rhodium structure of a conventional supported metal catalyst, Rh/γ-Al_2O_3.

The quartz microreactor system and the conditions of the X-ray beamline (ID24 at the ESRF) and also the data analysis techniques have been previously described.[2] Typically acquisition of a spectrum took 300–400 ms, spectra being recorded every 2–3 seconds. In Fig. 1 we show the Rh K-edge EDE-derived EXAFS from a 4 wt% Rh/γ-Al_2O_3 sample reduced *in situ* in a flow microreactor to 573 K under 4% H_2/He (a), and (b) that derived after exposure to 4% NO/He at 313 K for 5 seconds. Considerable changes are evident even after a short exposure. Data analysis indicates an initial state with a Rh site with ~8 Rh neighbours (Rh–Rh 2.68 Å) and ~3 non-nearest neighbours (Rh···Rh 3.75 Å). After exposure for 5 seconds, three shells are apparent: ~1 N at 1.78 Å, ~2 O at 2.05 Å and ~2 Rh at 2.72 Å. There are parallels with the oxidised centres, which are also produced after exposure to O_2,[3] the short Rh–N shell indicates some structural differences. In addition regeneration of metal on subsequent exposure to H_2/He is considerably slower, only occurring above *ca.* 390 K (see supplementary Fig. S2 ESI†).[3] Starting from either very small particles, $N_1^{\text{Rh–Rh}} = 4$ (~6 atoms), or larger ones, $N_1^{\text{Rh–Rh}} = 8.1\ (\pm 0.8)$ (*ca.* 40 < Rh atoms < 200),[4] affords a very similar product.

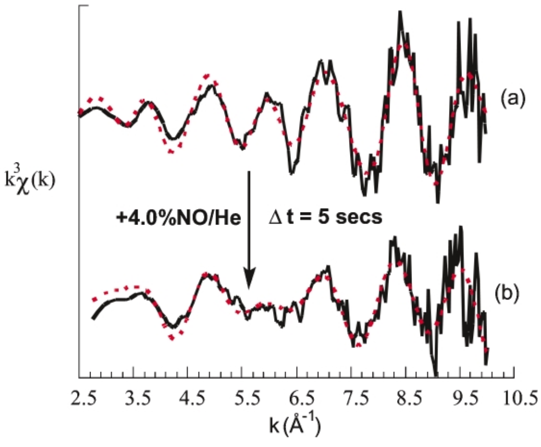

Fig. 1 Rh K-edge EDE derived k^3-weighted EXAFS data from a 4 wt% Rh/Al_2O_3 sample: (a) after *in situ* reduction to 573 K in 4% H_2/He and cooling to 313 K (spectra taken under He flow of 6 ml min^{-1}), and (b) after exposure to 4% NO/He for *ca.* 5 seconds. Black and red lines, respectively, indicate experiment and theoretical fits derived from spherical wave analysis in EXCURV98.[11]

Fig. 2 shows the temporal variation of the white line intensity, and the intensity of an EXAFS feature (the location of these points is shown in the ESI†), observed to increase and diminish respectively during the reaction. Data are shown for three cases: Rh particles showing $N_1^{\text{Rh–Rh}}$ of 4 (T_{red} = 313 K) during exposure of 4% NO/He (black) and CO (blue) at 313 K; and for Rh particles showing $N_1^{\text{Rh–Rh}}$ = 8 (T_{red} = 573 K) during exposure to 4% NO/He (red). It is well known that CO can disperse very small rhodium particles (CN ≤ 4) over longer timescales but it is clear that, under the conditions used here, CO fails to elicit any change in the observed Rh EXAFS, even for the most dispersed Rh sample.[5] NO diluted in He, however, effects rapid changes in the spectra derived from each supported system accompanied by a transient but pronounced (12.5 (±2.5) K) exotherm (Fig. 3). Coincident with this temperature rise, and

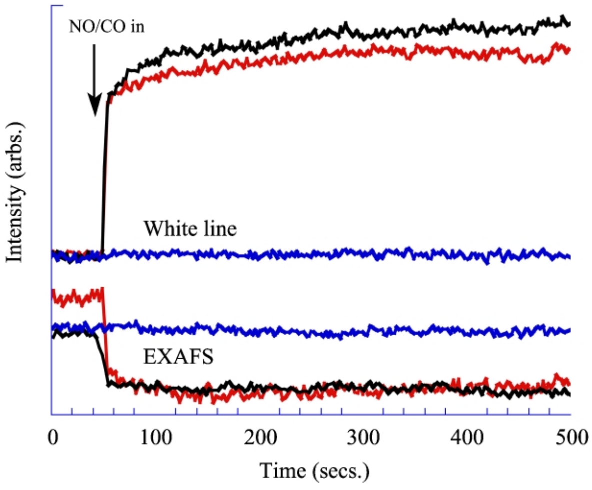

Fig. 2 Temporal response of the Rh K-edge white line and an EXAFS feature observed in the raw data 265 eV post edge (derived from 255 sequential EDE spectra (360 ms, 1 spectrum every ~2.5 seconds). Spectra obtained during switching of gas feed from He to 4% NO/He for pre-reduced samples showing $N_1^{\text{Rh–Rh}}$ = 4 (black) and 8 (red). The blue curves are those derived from gas switch from He to 4% CO/He (blue).

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† Electronic supplementary information (ESI) available: data showing monitoring positions in Fig. 2 and data showing reduction of the NO oxidised Rh adduct on alumina. See http://www.rsc.org/suppdata/cc/b1/b106846f/

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DOI: 10.1039/b106846f

the initial adsorption of NO, the evolution of mass 28 is observed followed by mass 44 (Fig. 3). Analysis of the evolution of minor mass fragments (12, 14, 22, 26, 32, and 42) indicates that these features are due to N_2 and N_2O respectively, with minor contributions from species such as O_2, CO, CN, CNO and CO_2. The approximate levels of NO uptake may be calculated from these experiments, and expressed in terms of NO/Rh atoms initially present. This yields an estimate of NO uptake of *ca.* 1.5 (±0.26) NO/Rh. The sensitivity of the mass spectrometer toward N_2O (44) and N_2 (28) (relative to NO) allows us to estimate that approximately 0.1 NO/Rh are reacted to yield the N_2 observed and *ca.* 0.14 NO/Rh are subsequently reacted to form N_2O. The remaining 1–1.2 NO/Rh are retained on the catalyst.

Many previous studies on similar systems (utilising vibrational spectroscopies)[6] have indicated the predominant formation of a linear Rh–NO^+ species, although contributions from other nitrosyls, such as $Rh(NO)_2$ are also observed. The EXAFS obtained from our experiments is consistent with the predominant formation of an oxidic Rh phase with a central core comprising of two (surface) oxygen bonds and, on average, a single nitrosyl species surrounding the Rh. The analysable datalength and the intrinsic noise associated with the data do not permit absolute confirmation of the nitrosyl species formed.

The rapid, exothermic reaction of Rh/γ-Al_2O_3 with NO must involve dissociative chemisorption to afford N_2 and N_2O. Since the sample bed is essentially solid Al_2O_3 ($C_p \sim 79$ J mol^{-1} K^{-1} [6]) the energy release may be estimated from the observed exotherms. For a typical sample, this yields a value of 0.16–0.23 J (20 mg sample, exotherm ~ 10–15 K). If this energy release is primarily due to dissociation of NO on the Rh particles, we can estimate that the bed temperature rise equates to a potential microscopic heating of the supported particles of *ca.* 640–960 K (assuming a C_p of bulk Rh[7]). Further, the level of NO dissociation can be calculated from the N_2 desorption; from this, the dissociative heat of adsorption (ΔE_{diss}) of NO may be estimated, as 300–400 kJ mol^{-1}. Estimates of ΔE_{diss} NO for Rh single crystals from both experiment[8] and theory[9] are also of the order of 300–400 kJ mol^{-1}.

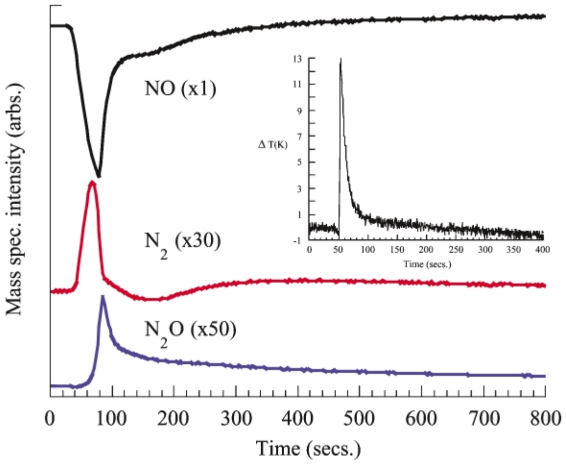

Fig. 3 NO uptake and major gas (N_2 and N_2O) evolution during switch to 4% NO/He gas feed over the Rh/Al_2O_3 sample previously reduced *in situ* in 4% H_2/He to 573 K along with the observed variation of sample bed temperature (ΔT, inset). The switch to a NO/He feed occurs at 60 seconds, and spectra are shown after subtraction of a null response to an identical gas switch over the reacted sample bed. The mass and scaling factor for each trace are indicated.

The extent and rapidity of the NO induced fragmentation of these supported Rh particles are in excess of those observed for any disruptive process previously reported. The source of these changes lies in the balance between the dynamics of molecular dissociation on the supported particles, and the processes available for the dissipation of that energy thus released from the particle into its surrounding medium. The consequences for mechanistic studies of highly dispersed oxide-supported heterogeneous catalysts are considerable. Clearly, structure reactivity relationships, like between *facile* (or structure insensitive) and *demanding* (structure sensitive) reactions,[10] based on the surface area measurements and catalytic reactions carried out under different conditions, may be problematical. With metal nuclearities changing within a few seconds under mild conditions, the active sites of high dispersion heterogeneous catalysts cannot be viewed as being located on monolithic particles.

This work is dedicated to the memory of the late Dr Judith Corker. This work was funded under the Catalysis and Chemical Processes (CACP) initiative of the EPSRC. The EPSRC is also thanked for postdoctoral funding to M. A. N. and ICI for postdoctoral funding to S. G. F. We would like to thank the ESRF for providing access to the synchrotron. The authors are also extremely grateful to Bruce Hancock, John James, Melanie Hill, Ralph Wiegel, and Sebastian Pasternak for their technical expertise. Professor R Schlögl is also thanked for the generous provision of the mass spectrometer facility available on ID 24.

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